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(54) Compositions containing chlorine and/or hypochlorite together with an aliphatic peracid for use in disinfection

(57) Chlorine and hydrogen peroxide react with each other destructively, with the result that a combination of them is less effective as a disinfectant than the chlorine by itself. It would be desirable to locate a peroxygen/chlorine combination that ameliorated or overcame that disadvantage.

Advantageously, cooperative disinfection occurs between chlorine and/or hypochlorite with a low molecular weight aliphatic peracid such as peracetic acid, and the weight ratio of the disinfectants often falls in the range of 1:5 to 1:30. The beneficial effect is apparent even in the presence of substantial residual amounts of hydrogen peroxide remaining by virtue of the method of production of the peracid:

Solid surfaces or liquid media, particularly recirculating industrial water can be treated with the combination of disinfectants.

Cl + POAA
low H₂O₂

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Disinfection

The present invention relates to disinfection and particularly to processes for disinfection in which a combination of disinfectants is employed and compositions
5 containing such a combination.

Hitherto, many different types of disinfectants have been proposed, of which two types that are widely available are based respectively upon their active chlorine content and upon their active oxygen content. It would be
10 advantageous if both types of disinfectant could be employed simultaneously, but it has been recognised for a long time that active oxygen compounds and active chlorine compounds, or more specifically chlorine compounds containing free chlorine or oxychlorine species like hypochlorite react
15 together to their mutual destruction. This reaction was reported by A E Cahill and H Taube in J. Am Chem Soc, 74,2312 (1952). It was confirmed subsequently in German patent application 2 443 680 to Du Pont in which hydrogen peroxide was added to an effluent containing hypochlorite in
20 order to remove it from solution. The mutually destructive interaction of the two types of disinfectants has also been recognised in the field of disinfection. Thus, in US Patent 4 239 622 assigned by J W Ridgeway to Interlox Chemicals Limited rapid and mutual destruction of the free chlorine
25 residual and hydrogen peroxide in an aqueous medium was demonstrated. Subsequently, in USP 4 243 525, assigned to FMC, and the corresponding EP-A- 46 459, a multi-stage process for disinfecting water is disclosed in which addition of hydrogen peroxide precedes addition of excess
30 chlorine, and indeed, it is clearly stated that the chlorine

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reacts with the hydrogen peroxide. It has now been confirmed in background studies conducted in the context of the instant invention that the mutual destruction of the chlorine and peroxide disinfectants does in fact result in
5 impaired disinfection.

In view of their chemical incompatibility, the active oxygen and active-chlorine disinfectants have been regarded as alternatives and except for the destructive reasons outlined above, not considered for use in combination.

10 Surprisingly, it has now been found that a class of active oxygen compounds exists which can mutually coexist with free chlorine containing compounds for at least a sufficient period that both types of disinfectant can continue to function effectively.

15 According to the present invention there is provided a process for disinfection of a surface or liquid medium by respectively intimate contact therewith or incorporation therein of a disinfectant characterised in that the disinfectant comprises an effective amount of a combination
20 of chlorine and/or hypochlorite with a low molecular weight aliphatic peracid.

According to a related aspect of the present invention there are also provided liquid compositions containing the combination of chlorine and/or hypochlorite with the low
25 molecular weight aliphatic peracid. Such compositions can be brought into contact with solid surfaces or introduced into liquid media that it is desired to disinfect.

One of the features of the present invention that highlights the particularly surprising nature of the
30 invention is the fact that low molecular weight aliphatic peracids, as made, normally contain a substantial residual concentration of hydrogen peroxide, often in equilibrium with and in a similar amount to or sometimes even more than that of the aliphatic peracid itself. Accordingly, it would
35 be the normal prediction that such residual hydrogen peroxide would participate in the expected and unwanted manner with the chlorinaceous species, and indeed could even

result in the reversion of the peracid to hydrogen peroxide by operation of the re-equilibration reaction on loss of hydrogen peroxide. Even when the aliphatic peracids employed herein retain such aforementioned substantial residual proportions of hydrogen peroxide, the beneficial cooperation between the two types of disinfectants is retained. In other words, if, as we may reasonably postulate, some mutual destruction of the disinfectants does occur, we can explain the results on the basis that it does so at such a rate that the negative effect of loss of disinfectant is cancelled out and compensated for by synergism in disinfection from the residual disinfectants. It will be understood, however, that the foregoing explanation is provided by way of assistance and to rationalise the results obtained and that the instant invention is not dependant in any way on the veracity of that explanation.

The low molecular weight aliphatic peracids employed in the present invention include in particular monobasic acids containing up to 4 carbon atoms, and especially peracetic and perpropionic acids. These peracids can readily be prepared by reaction between hydrogen peroxide and the corresponding aliphatic acid or less usually with the corresponding acid anhydride.

The two disinfectants can be employed in a wide range of weight ratios. In many instances these will be in the range of from 1:1 to 100:1 w/w of peracid:chlorine, and in some preferred embodiments the ratio is in the range of 5:1 to 30:1 w/w.

The actual concentrations of the disinfectants employed will depend upon the extent of disinfection desired, the extent of contamination of the medium to be disinfected, and the physical conditions in which disinfection is to be effected, such as the temperature of the medium, and the period of time available for the disinfection to occur. For the treatment of aqueous media, including industrial process water, recycled water and water intended for discharge into

public watercourses, the concentration of the peracid is often selected within the range of from 1 to 50 part per million parts by weight of aqueous medium, (ppm) and in preferred embodiments is often from 4 to 20 ppm. The concentration of chlorine disinfectant for the same medium is often selected in the range of from 0.1 to 25 and especially from 0.2 to 5 parts of chlorine per million parts by weight of the aqueous medium. These ranges correspond quite closely to and overlap with the lower parts of the ranges of the same disinfectant that could be contemplated in the absence of the other type.

The disinfectant combination can be employed to treat solid surfaces, generally, and these can include surfaces of wood, metal, plastics, resins, paper, glass, and ceramics. The process can also be used to treat aqueous media containing a substantial amount of domestic, industrial and/or municipal waste solids, i.e sewage and the sludge separated therefrom.

The process is preferably effected by introducing the two disinfectants separately into the liquid medium to be disinfected or into the solution to be employed for disinfecting a solid surface, and accordingly premature interaction which might occur between the disinfectants if mixed in very concentrated form is avoided. The benefit of employing the mixture of disinfectants is that the concentration of each component can be employed at a lower level than would be the case if it were used by itself. Thus, the advantage of being able to use less chlorine is that there is less environmental impact from chlorine residuals, and the advantage of employing less peracid is that the process is rendered correspondingly cheaper than if all the chlorine were replaced by peracid. In some cases the reduction in concentrations is even greater than on a purely summative basis and then the saving can be even greater. Whilst the treatment with both disinfectants can be effected from the start, it is an alternative method on occasions to commence disinfection with one of the

disinfectants only and introduce the other intermittently, for example in response to an increase in the numbers of micro-organisms in or on the medium being disinfected. By so doing, then the increase in micro-organism numbers can be controlled without recourse to the use of an increased concentration of the first disinfectant, but by addition of the second disinfectant. In this latter sort of occasion for using the invention process, it would often be the case that chlorine or hypochlorite is the disinfectant that is constantly employed and a peracid, especially peracetic acid is the disinfectant that is added in response to increase in micro-organism numbers. It is a further benefit of the combination that it is able to treat simultaneously a wider spectrum of micro-organisms than either disinfectant can treat alone at the same concentration.

When the two disinfectants are introduced separately into a liquid medium, or on mixing both with water to form a combined disinfectant, each can be in the normal commercially available form or a variation thereof. Thus, the peracid can be employed as an aqueous solution containing an equilibrated amount of the precursor carboxylic acid, hydrogen peroxide, and water as well as the peracid and equilibration catalyst. The concentration of peracid before dilution is normally in the range of 1 to 45% w/w peracid, depending upon the ratio of reactants used in the preparation of the peracid. The actual concentration can be chosen by the user of the invention process at his discretion. The more concentrated solutions have the advantage that an effective amount of peracid can be obtained from a small volume of solution, whereas the use of the more dilute solutions advantageously provides a less aggressive smell. The chlorine species is most conveniently employed as a solution of an alkaline earth metal hypochlorite, especially sodium hypochlorite or by introduction of gaseous chlorine, the choice being at the discretion of the user.

The invention process is normally carried out without

need to adjust the temperature of the medium being disinfected. which normally will fall within the range of 0 to 70°C and in many instances in the preferred range of from 10 to 50°C.

5 The invention process can be carried out conveniently in media having a wide range of pHs, but is most effective in the region of mildly acidic through to approximately neutral solutions, such as pH 4 to pH 8. Having outlined the invention in general terms, specific embodiments will now be
10 described more fully by way of example only.

In the Examples and comparisons, the test procedure for determining the effectiveness of each of the disinfectants or disfectant combinations was the same, and it was as follows:-

15 The strains of micro-organisms employed in the tests were respectively:-

Escherichia coli	ATCC 11229	(Coli)
Pseudomonas aeruginosa	ATCC 15442	(Pseud)
Staphylococcus aureus	ATCC 6538	(Staph)
20 Streptococcus faecalis	ATCC 10541	(Strep)

Sub cultures were taken from stock cultures on agar slants that had been kept at 4°C in a refrigerator and were 24 hours old when employed as the innoculum. The cultures were removed from their culture medium by centrifugation for 10
25 minutes, washed with sodium sulphate solution and resuspended in sodium sulphate solution.

For each species of micro-organism, the concentration of viable cells in the innoculum was determined by a serial dilution technique. Two samples (1ml) of appropriately
30 diluted innoculum are dosed into Petri dishes into which is also added molten agar at 46°C, and the plates incubated at 37°C for 48 hours and the number of colonies counted. The normal initial concentration was between 100 and 300 colonies per plate following the dilutions, corresponding to
35 $1-3 \times 10^8$ cfu per ml of the innoculum.

In each test to determine the activity of the disinfectant or mixture of disinfectants, a solution at

double testing strength was freshly prepared and 5ml was then diluted with distilled water, 4ml, and 1ml of an aqueous sodium sulphate suspension of the selected micro-organism with the result that the initial concentration of the micro-organism in the test solution was in excess of 10^6 colony forming units /ml. The solutions were kept at laboratory ambient temperature (usually in the range 20 to 25°C) for 5 minutes, whereupon a sample of 1 ml was withdrawn and diluted into the appropriate neutraliser solution (9 mls) to prevent any further interaction between disinfectant and micro-organism. After a further 5 minutes, samples were withdrawn, and where necessary serially diluted into sterile sodium sulphate solution. Two samples of the optionally diluted solution, each of 1ml, were inoculated into Petri dishes with agar and incubated in the same way as for the initial determination of micro-organism concentration. The numbers of colonies on the incubated plates were counted, and averaged, so that the post-disinfection concentration of viable micro-organisms was obtained.

By comparing the post-disinfection count with the initial count, and making allowance for the extent to which the samples had been diluted, the extent to which the disinfectant has reduced the concentration of viable micro-organisms was calculated and expressed as the LRF, i.e the ratio of the initial concentration to the post-disinfection concentration expressed in the form of a logarithm base 10.

Chlorine was introduced in the form of a standardised aqueous sodium hypochlorite solution, nominally of about 10% w/w, in an amount sufficient to provide the specified concentration of available chlorine (as Cl), the hydrogen peroxide was employed as a 35% w/w aqueous solution in an amount sufficient to provide the concentration of H_2O_2 specified and peracetic acid (abbreviated to PAA) was employed as a solution containing approximately 15% w/w peracetic acid, 14% w/w hydrogen peroxide and the balance water and acetic acid, available from Interox under the

trademark PROXITANE 1507.

When hydrogen peroxide was used by itself, the neutralising solution comprised a mixture of 1 part by volume of component a) with 9 parts by volume of component b). Component a) was a solution of Catalase, Sigma C-10, 2.5g in 1 litre demineralised water that had been sterilised by membrane filtration, pore size 0.45um, and component b) was demineralised water that had been sterilised by heating to 121°C for 15 minutes (Sdmw).

10 When peracetic acid was employed, either alone or with chlorine, the neutraliser consisted of a mixture of 1 part by volume of component a) with 9 parts by volume of component c), the latter obtained by dissolving sodium thiosulphate pentahydrate, 50g, Analara (^{Reg.}Trade Mark) in 1
15 litre of Sdmw.

When chlorine was used by itself, the neutraliser (component d) consisted of a phosphate buffer solution, 10 mls, 1-alpha-phosphatidylcholine, Sigma P-5638, 3g, nonionic surfactant, TWEEN (^{Reg.}Trade Mark) 80, 30mls, L-histidine, Sigma
20 H-8000, 1g, sodium thiosulphate pentahydrate, Analara, 5g in Sdmw, 960 mls. The phosphate buffer solution consisted of potassium dihydrogen phosphate, Analara, 34g, demineralised water, 500mls, sodium hydroxide solution, 1M, to pH 7.2 +/- 0.1, and Sdmw balance to 1 litre.

25 When chlorine and hydrogen peroxide were employed together, the neutraliser consisted of the mixture of 1 part by volume component a) with 9 parts by volume of component d).

The results are summarised in the Table below.

The Table

Ex/ Comp No.	Disinfectant Concentration			Effectiveness of disinfection				
	mg/L			LRF				
	Cl	H ₂ O ₂	PAA	Coli	Pseud	Staph	Strep	
5								
	C1	0	0	4	<1.5	<1.6	<1.1	<1.5
	C2	0	0	8	>6.2	3.2	1.5	1.5
	C3	0	0	11	>6.2	3.7	2.7	2.0
	C4	0	0	15	>6.2	5.6	>6.1	5.2
10	C5	0	14	0	<1.5	<1.3	<1.1	<1.2
	C6	0.5	0	0	<1.2	<1.6	<1.1	<1.5
	7	0.5	0	4	5.4	3.0	<1.1	<1.5
	8	0.5	0	8	6.2	3.5	>6.1	<3.5
15	9	0.5	0	11	>6.2	4.2	>6.1	5.3
	10	0.5	0	15	>6.2	6.3	>6.1	>6.2
	11	0.5	14	0	<1.2	<1.3	<1.1	<1.2
	C12	1.0	0	0	3.4	2.6	2.8	3.1
20	13	1.0	0	4	<3.2	2.2	3.5	<3.5
	14	1.0	0	8	>6.2	4.9	6.4	>6.2
	15	1.0	0	11	>6.2	6.6	>6.1	>6.2
	16	1.0	0	15	>6.2	>6.3	>6.1	>6.2
	C17	1.0	14	0	<1.2	<1.3	<1.1	<1.2
25								

The results fall into three categories. In the first category, the results for LRF are quoted as <n. In those runs the number of viable micro-organisms at the end of the test was so large that the colonies on the agar plates fused so that further solution dilution before plating would have been needed to establish the actual disinfectant effect attributable to the disinfectants. It can, however, be deduced that the disinfection capability of the disinfectants was lower than the figure quoted. In the second category of tests, a measurable number of viable micro-organisms survived, and the extent of the reduction in numbers is given by the size of the LRF. In the third

category, appearing as >n, there were no survivors in the test, so that the disinfectant was capable of effecting a reduction in the numbers of the micro-organism of at least the original population.

5 From the Table, and in particular by comparing Cl7 with Cl2, it will be observed that the combination of hydrogen peroxide and chlorine disinfectants was antagonistic, i.e. the net result was worse than employing chlorine alone, which was clearly the better disinfectant. From Cl2, with
10 chlorine in its worst case, only 0.25% of the micro-organisms remained viable whereas Cl7 shows that when hydrogen peroxide was added as well the degree of disinfection was at least 20 times worse, and in fact was no better than adding hydrogen peroxide alone. A comparison of
15 C6 with Cl1 is consistent with the foregoing, and at the very least does not show any additive effect between the two disinfectants.

On the other hand, it will be seen by comparing the results obtained with peracetic acid solution alone, Cl to
20 C4 and chlorine alone, C6 and Cl2 with the combination of the two together, Ex7 to Ex10 and Ex13 to Ex 16, that the two disinfectants cooperated despite the presence in the peracetic acid solution of the same amount of hydrogen peroxide, so that the antagonistic effect of chlorine and
25 hydrogen peroxide had to be overcome first. Thus, if Ex7 is studied, it will be apparent that for both *E coli* and *Pseudomonas aeruginosa* the disinfection was significantly greater than for either disinfectant alone, and indeed most probably such a combination represented synergistic
30 disinfection. Likewise, if Ex8, Ex9, Ex13 and Ex14 are studied, it will be seen for the two other micro-organisms, *Staphylococcus aureus* and *Streptococcus faecalis* that once again synergistic disinfection is demonstrated. The other runs with the invention combination continue to show that
35 the disinfectant capability of the better disinfectant is usually preserved or enhanced by the presence of the other disinfectant.

Claims:-

1. A process for disinfection of a surface or liquid medium by respectively intimate contact therewith or incorporation therein of a disinfectant characterised in that the disinfectant comprises an effective amount of a combination of chlorine and/or hypochlorite with a low molecular weight aliphatic peracid.
2. Liquid compositions containing the combination of chlorine and/or hypochlorite with the low molecular weight aliphatic peracid.
3. A process or composition according to claim 1 or 2 characterised in that the weight ratio of peracid to chlorine is selected in the range of from 1:1 to 100:1.
4. A process or composition according to claim 3 characterised in that the weight ratio of peracid to chlorine is selected in the range of from 5:1 to 30:1.
5. A process or composition according to any preceding claim characterised in that the concentration of peracid is selected in the range of 1 to 50 ppm w/w and the concentration of chlorine is selected in the range of from 0.1 to 25 ppm w/w.
6. A process or composition according to any preceding claim characterised in that the disinfection is conducted at a pH of from pH 4 to pH 8.
7. A process or composition according to any preceding claim characterised in that the peracid is peracetic acid.
8. A process for disinfection employing in combination an organic peracid and chlorine substantially as described

herein with respect to any one of Examples 7 to 11 or 13 to 16.

9. A disinfectant composition containing in combination an organic peracid and chlorine substantially as described herein with respect to any one of Examples 7 to 11 or 13 to 16.